IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No.: 22080.002

In re Application of

Luis Alfredo Diaz Chavez Examiner: **Rebecca Y. Lee**

Serial No.: **10/565,715** Art Unit: **1793**

Filing Date **06/12/2006** Conf. No.: **7944**

For **CALCO-MAGNESIAN AQUEOUS SUSPENSION AND METHOD FOR THE PRODUCTION THEREOF**

DECLARATION

Mail Stop: Fee Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

My name is Marc PELLETIER, I am an engineering graduate of "Polytech'Orleans", section "Minerals and ores processing", since 1985, and Head of the Analytical Laboratory and Technical Assistance of Lhoist R&D Center, since 2001.

I have read the Specification in the above pending application and am familiar with the claims in the case. I am also familiar with the *Huege et al.* reference being cited by the Examiner (US 5,616,283).

I performed a series of comparative laboratory tests measuring the BET surface area of a sample made according to the teachings of the *Huege et al.* reference and comparing it with the BET measurements of material made according to the teaching of the presently claimed invention.

Document #: 14638
Version#: 1

Please find below the results for materials produced according to Example 3 of the *Huege et al.* reference, (US 5,616,283):

For the "$Ca(OH)_2$", two different hydrated limes of industrial grade are used : Limes A and B. In both cases, a delay of 1 hour is left between the mixing of the components according to Example 3 of the *Huege et al.* reference and the filtration of the milks of lime (lime slurries) obtained to recover the solid for analysis purposes.

Please find below the measurements of BET specific surface area.

Type of lime	BET specific surface area	Solid from milk of lime (after filtration/drying) according to Example 3
Lime A	15 m^2/g	19 m^2/g
Lime B	18 m^2/g	20 m^2/g

I am attaching to this Declaration a copy of the Oates treatise, which is well known in the lime industry, showing that industrial hydrated lime typically has a BET specific surface area between 15 and 20 m^2/g, which evidences the fact that Lime A and Lime B above fall within the scope of such limes of industrial grade.

It is evident from the above test measurements of the BET specific surface area that, starting from standard (common) industrial $Ca(OH)_2$, the material made according to the teaching of the *Huege et al.* reference does not show a BET specific surface area lower than 10 m^2/g, as in Applicant's claimed invention.

Further for a lime prepared according to the teachings of the presently claimed invention, the following measurements were made:

Type of lime	BET specific surface area	Solid from milk of lime (after filtration/drying) according to Example 3
Lime C	7 m^2/g	8 m^2/g

I would further draw the Examiner's attention to the fact that the Oates treatise, attached, also teaches the principle that: it has been recognized for many years that the particles of calcium hydroxide in "milks of lime" have higher surface area (up to $30m^2/g$) than normal hydrated time (typically 15 to $20m^2/g$). You can also find information in the treatise regarding the fact that "surface area" is BET specific surface area. As a matter of consequence, it is clear that the results of the tests are totally in line with and support such a statement, (that hydroxide from milk of lime BET specific surface areas are higher than the BET surface area of dry starting hydroxide), even if the presence of additives (such as dispersants and NaOH) as described in the *Huege et al.* reference may influence the results.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Marc PELLETIER

Signature

April 28, 2010

Marc PELLETIER

ATTACHMENT 2
Appl. Serial No. **10/565, 715**
Filed **06/12/2006**

J.A.H. Oates

Lime and Limeston

Chemistry and Technology, Production and Uses

WILEY-VCH

Weinheim · New York · Chichester
Brisbane · Singapore · Toronto

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Cover picture: A Beckenbach Annular Shaft Kiln
(courtesy of Beckenbach Wärmestelle GmbH)

Library of Congress Card No. applied for
A catalogue record for this book is available from the British Library

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Oates, Joseph A. H.:
Lime and limestone : chemistry and technology, production and uses /
J. A. H. Oates. – Weinheim : Wiley-VCH, 1998
ISBN 3-527-29527-5

Printed on acid-free and low chlorine paper

Composition: Kühn & Weyh Software GmbH, D-79015 Freiburg
Printing: betz-druck GmbH, D-64291 Darmstadt
Bookbinding: Großbuchbinderei J. Schäffer, D-67269 Grünstadt
Printed in the Federal Republic of Germany

Preface

The Lime and Limestone Industries are dynamic industries, with new prodt methods, new products and new uses continually being developed. The particularly interesting and challenging, because of the wide variety of pro made, and the even wider range of applications.

Both industries are being profoundly affected by the general requireme improve environmental performance. On the one hand, this presents a chall which is leading to heavy capital investment, mergers and even closures. O other hand, it presents new opportunities to supply environmental control ucts.

Another major development, which affects both producers and custom the widespread reduction of manning levels. While this increases productivit profitability, it places greater pressures on everyone to cope with less tec assistance than in the past. In consequence, there is a need to develop and b en individual expertise, and to have improved access to up-to-date informati

One of the aims of producing this book is to present an integrated perspe of the Lime and Limestone Industries, and to indicate how they have been still are being shaped by customer-led requirements.

- It describes the many complex interactions, relating to product quality. exist between suppliers and customers, both within and outside the Indus This should help production personnel in the Industries to appreciat impact of their actions and decisions on their customers.

- For users of lime and limestone products, it seeks to give an understandi the factors which affect product quality and the ways in which the pro interact with the processes in which they are used. It also indicates ho Lime and Limestone Industries control product quality, and what ac might be taken to tailor quality for a particular application.

- It may also provide a basis for constructive dialogue between supplier customers, thereby facilitating the development of new and improved ucts.

The formation of the European Union is leading to the preparation of a number of application-specific Standards, specifying both product quality an methods. Combining the diverse products and practices used in so many tries, each with its own traditions, is proving to be both demanding and stim ing. While many relevant CEN Standards have already been published, others are still in preparation at the time of going to press.

Coarse grit, which consists of calcium carbonate, any unslaked quicklime and water-burned hydrate is retained by the weir. It may be removed at intervals (e.g. at the end of shifts) by opening a "purge hole" in the weir or by lowering the weir. In such cases, the grit is generally rejected to tip. Alternatively, the grit may be removed continuously from the hydrator by a "purge paddle" which lifts it over the weir. In this case, the grit is removed from the "raw hydrate" by air classification or screening. Such "hydrator rejects" are either tipped, blended in a controlled manner into selected products, or sold as agricultural lime.

In the finishing stage, residence time is provided to:

a) reduce the level of free lime, and
b) allow surplus moisture to evaporate.

The plant is kept under slight suction to prevent dust emission and to maintain a low flow of air through the finishing stage to facilitate drying. The moisture content of the "raw hydrate" on discharge from the finishing stage is generally up to 1 %.

20.4.4 The Classification Stage

A large number of variations of classification plant have been used successfully. The choice depends largely on the quality of the feed lime(s) and the required quality of the product(s). In the lay-out shown in Fig. 20.1, the raw hydrate is fed to the primary air classifier, which can be adjusted to give a cut size meeting the required particle size specification.

Oversized particles rejected by the classifier (the primary tailings) consist of varying proportions of unburnt limestone, hydrated quicklime and gritty hydrate. They are generally processed in one of three ways.

a) The simplest approach is to mill the primary tailings, which are then fed to the secondary air classifier. The resulting fine fraction (secondary fines) are either blended with the primary fines or used to produce a less pure grade (e.g. for building applications [20.5]). The coarse fraction from the secondary classifier, (secondary tailings), are recycled to the mill.
b) If the secondary fines contain unacceptable amounts of free CaO, they may be recycled to the hydrator.
c) Where it is required to use the classification plant to remove some of the unburnt limestone, various options exist for isolating a $CaCO_3$-rich fraction. One option is to pass the primary tailings through a beater mill, which is designed to preferentially reduce the particle size of the relatively soft quicklime and gritty hydrate, leaving the size of the harder limestone substantially unchanged. Air classification of the milled product produces a lime-enriched secondary fines fraction and a carbonate-enriched secondary tailings fraction. The latter may be tipped, or sold as agricultural lime. The secondary fines can be transferred to a product bunker, or, if they contain excessive free lime, recycled to the hydrator.

20.5 Control of Hydrating Plant

The primary controls are the feed rates of the water and quicklime to the plant. These should be designed to give high levels of consistency (e.g., to better than ±0.5 %), so that the required level of excess water in the hydrate can be maintained to within the required range. The preferred approach is to feed a constant weight of lime and to adjust the water flow rate to achieve the required temperatures and moisture contents [20.5]. Variations in the quality of the feed lime (e.g. in the reactivity or % $CaCO_3$) can change the water requirement significantly. Precautions should be taken to minimise such variations, particularly when several grades of lime are fed to the plant.

For optimum control, the temperatures of the raw hydrate should be monitored as it passes through the hydrator and finishing stage. The temperature profile depends on the level of excess water and on the reactivity of the lime. For a given feed lime, a decrease in temperature towards the discharge of the hydrator and in the finishing stage is indicative of an increase in moisture content, and vice versa. The current drawn by the motors driving the paddles can also be indicative of moisture content.

It is particularly important to limit the level of excess moisture in the plant, as the handling characteristics of hydrated lime deteriorate rapidly when the moisture content rises above 1.5 or 2 %. Excessive levels of moisture result in blockages within the plant and hold-ups in bunkers.

Various techniques are used for determining the moisture content of the raw hydrate. They include visual inspection, a rapid "carbide" test method, infra-red moisture meters and conductivity probes. The latter can be built into the wall of the finishing stage vessel [20.5].

The grading of the fines streams may be determined by air-jet sieving and adjusted by varying either the speed or the settings of the air classifiers. Some customers require other properties to be controlled such as the specific surface area (measured by air permeability [20.6]) and the settling rate of milks of lime produced from the hydrate.

20.6 Production of High Surface Area Hydrated Limes

20.6.1 General

In the 1980's the opportunity for using hydrated lime to remove acid gases from processes such as incinerators and small boilers was recognised. However, trials showed that relatively large excess of commercially available hydrate had to be added to reduce the acid gas concentrations to the required levels. It was postulated that increasing the *effective* surface area would increase absorption efficiencies. The challenge was how to produce a hydrate with significantly improved properties.

It has been recognised for many years that the particles of calcium hydroxide in "milks of lime" have higher surface areas (up to 30 m^2/g), than normal hydrated lime (typically 15 to 20 m^2/g). However, the cost of drying a milk to produce a high surface area hydrate would be excessive. While milling hydrated lime improves its plasticity [20.7], it does not increase its specific surface area significantly, presumably owing to the production of relatively dense agglomerates.

Research has shown that hydrates with high specific surface areas could be produced by slaking with water-alcohol mixtures, and with aqueous solutions of sugar, lignosulfonate, or amine derivatives [20.8–20.10]. This effect was regarded as little more than a curiosity until the requirement for a high surface area hydrate was identified. Two approaches have resulted in products which have significantly larger effective surface areas. They are described below.

It should be noted that these developments are on-going. Questions are still being asked as to how the effective surface area correlates with:

a) the specific surface area, as measured by the BET (Berkland Eyde and Teller) technique,
b) the total volume of the pores,
c) the size distribution of the pores,
d) the particle size, and
e) the degree of agglomeration.

20.6.2 Hydration with a Methanol-Water Mixture

The laboratory work leading to this development is described in [20.11]. Ground quicklime is used to avoid the need to classify the product. It is mixed with a water-methanol solution, the composition and volume of which provides sufficient water for the hydration reaction and sufficient methanol to remove, by evaporation, the heat of hydration (the boiling point of methanol is 65 °C)

When most of the lime has hydrated, most of the water has reacted and most of the methanol has evaporated, so that the mixture passes through a solid phase. Subsequent hydration and evolution of methanol vapour and steam causes the mixture to break down into a finely divided powder.

The process can be regarded as consisting of six stages [20.12, 20.13].

a) In the mixing vessel, ground quicklime is mixed with the methanol-water solution (typically containing 60 % of methanol) at below 45 °C. The presence of the alcohol and the low temperature inhibit the hydration reaction.
b) The suspension is then heated to between 50 and 70 °C and transferred into the main reaction vessel, which is agitated by plough-type mixers.
c) In the vessel most of the water reacts with the quicklime and most of the methanol evaporates.
d) The partially hydrated solid is then transferred into the second reaction vessel.
e) In the second reaction vessel, which is also agitated, hydration proceeds to completion and the temperature rises to 95 to 110 °C. The resulting evolution of methanol vapour and steam causes the granules to break up into a fine powder.

f) The fully hydrated product then passes into a de-gasifier, which removes most of the residual methanol and water, using either a nitrogen purge or a partial vacuum. It is then discharged into a cooler from which it is conveyed to a storage silo.

The finished product has a specific surface area of 35 to 43 m^2/g. It is reported to have good handling properties, to disperse well, and to be significantly more effective at removing acid gases than normal hydrated limes [20.12].

Inevitably, the capital and operating costs of the plant are relatively high. Apart from the de-gasser, the equipment is kept at above atmospheric pressure by a supply of nitrogen to prevent the ingress of air. Methanol vapour, together with some steam, from the reaction vessels and the de-gasifier, is condensed and recycled. In view of the explosion hazard, the equipment has to be well engineered and all electrical equipment within the plant is of flame-proof quality.

20.6.3 Hydration with Aqueous Solutions

Details of this process are still largely confidential. An early patent [20.14] described the hydration of reactive, fine lime (e.g., less than 6 mm) with water in the presence of an amine/glycol additive. Specified compounds were mono-, di- and tri-ethyleneglycols and mono-, di- and tri-ethanolamines, and mixtures thereof. Hydrates with surface areas of 46 m^2/g were cited.

It is understood that the process has since been developed and that further patents are pending [20.17].

20.7 Performance Criteria for Hydrated Limes

A variety of test methods are available to characterise hydrated lime. As they all measure different parameters, the choice of the most appropriate method(s) depends on the application.

20.7.1 Chemical

The chemical activity of hydrated lime can be measured in at least three ways, namely by:

a) neutralising value ($CaO + Ca(OH)_2 + MgO + Mg(OH)_2 + CaCO_3$ + part of the CaO in silicates/aluminates),
b) available lime ($CaO + Ca(OH)_2$), and
c) water soluble lime ($CaO + Ca(OH)_2$ + part of $Mg(OH)_2$ and part of the CaO in silicates/aluminates).

High-calcium and dolomitic hydrated limes for use in building are classified in terms of their CaO and MgO contents [20.19].